1967

A determination of the rate of evaporation of zinc at atmospheric pressure.

Yu Ming Su

A DETERMINATION OF THE RATE OF EVAPORATION OF ZINC AT ATMOSPHERIC PRESSURE

BY

YU MING SU _ 1936

A

THESIS

submitted to the faculty of

THE UNIVERSITY OF MISSOURI AT ROLLA

in partial fulfillment of the requirements for the

Degree of

129567

MASTER OF SCIENCE IN METALLURGY

Rolla, Missouri

1967

Approved by

T. J. O'Keefe (advisor) Fred Kissinger

D. E. Vaughn Jr.

Earl J. Carlson

ACKNOWLEDGEMENTS

The author wishes to thank the University of Missouri at Rolla for providing the opportunities and facilities necessary for carrying out this investigation.

The author wishes to express his sincere appreciation to Dr. T. J. O'Keefe for suggesting the problem and for his guidance, consultation, and advice.

Sincere thanks are also due to Dr. F. Kisslinger, for his valuable suggestions and guidance.

The author is also indebted to the faculty of the department for their advice and the Blackwell Zinc Company, Blackwell, Oklahoma, for their financial assistance in support of this project.

ABSTRACT

Measurements of evaporation rates of zinc in three different residual gases, e. g., argon, carbon monoxide, and hydrogen at one atmosphere pressure, were made. It was found that the rate of evaporation of zinc in one atmosphere of argon was almost the same as that in carbon monoxide, while the rate in hydrogen was almost twice the rate in argon or carbon monoxide.

Measurements of evaporation rate of zinc in one atmosphere of argon-oxygen mixtures were also made. The evaporation rate was considerably reduced because the formation of the oxide film retards the zinc vapor escaping from the evaporating surface.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

Figures

LIST OF TABLES

I. INTRODUCTION

The smelting of zinc involves reduction of the oxide at temperatures above the boiling point of zinc. The reduced zinc is removed from the reaction mixture as a vapor and is subsequently condensed. This is sometimes called a distillation process. This zinc is sufficiently pure to market for some applications after merely remelting and casting into ingot form. However, for other applications a purer zinc is required and several companies refine the zinc in a fractional distillation process.

During the fractional distillation of zinc, two elements, lead and cadmium in particular, are volatile. Lead is less volatile. In a commercial purification process the separation of lead appears to be more of a problem than separation of cadmium.

There is still some question as to the correct value of the activity coefficient of lead in liquid zinc. This is important since it determines the theoretical amount of lead that would be expected to distill during the refining process. There are also indications that the presence of certain impurities has an effect on the rate of distillation of zinc, as might be expected. The actual mechanism or reason for this behavior is not known and probably merits further study.

Some of the factors affecting the rate of evaporation of zinc have been investigated and are reported in the thesis.

II. REVIEW OF THE LITERATURE

About forty years ago H. M. Cyr,[1] working in the Research Laboratories of the New Jersey Zinc Company, produced a few pounds of zinc of such purity that no other elements were detected in it by spectrographic analysis. This zinc contained less than 0.0010 per cent of metallic impurities. It was prepared by the vacuum distillation of liquid zinc. The vapor was condensed directly to the solid state on a graphite sleeve from which it could be readily removed.

The New Jersey Zinc Company[2] was the first to develop a continuous and integrated commercial unit in which zinc could be refined by a distillation process.

The impurities which generally occur in zinc can be divided into two types. One type contains the more volatile elements, such as cadmium and occasionally arsenic in small amounts, and the other the less volatile elements, such as lead.

Basically, the pyrometallurgical refining of zinc involves three steps: a) iron, copper and other metals having no appreciable vapor pressure at 907°C concentrate in the bath in which the impure zinc is boiled, b) lead, bismuth, antimony and other metals having boiling points above but closer to that of zinc are selectively condensed from the vapor boiled from the bath and c) cadmium and other impurities having lower boiling points than zinc are fractionally distilled by reboiling and subsequent condensation of the cadmium and other impurities from the vapor.

Equilibrium conditions between liquid and vapor in the zinc-cadmium system are shown in the phase diagram in Figure 1[3]. The vapor is richer in cadmium than the liquid with which it is in equilibrium. Thus, during distillation the cadmium is concentrated in the vapor phase at the top of the column while purified zinc is collected as a liquid at the bottom of the column.

The zinc-lead equilibrium diagram as given by Lumsden[4] is shown in Figure 2. The diagram shows that the degree of purification attained when zinc containing lead is vaporized is much greater than that attained with zinc contaminated with cadmium.

The equilibrium data, in a different form, on the zinc-lead system is presented by Robson[3]. He gives the boiling points of zinc-lead alloys as a function of alloy composition shown in Figure 3. The boiling point of a solution of zinc containing lead rises only a few degrees as the lead content increases from zero up to about 60 per cent. This means that a small amount of superheat can volatilize most of the zinc. The remaining alloy with a high lead content exerts a vapor pressure comparable to that of pure lead. Thus, one partial vaporization separates most of the zinc from most of the lead.

The degree of lead elimination resulting from the vaporization process is very important. Richardson[5] discusses this subject. At 907°C, the boiling point of zinc, the vapor pressure of zinc is 760 mm Hg and that of lead at the same temperature is 0.3 mm Hg. If the total pressure were one atmosphere and the lead solution were ideal, the partial pressure of zinc in the vapor, $p_{Zn(g)}$, at 907°C would be 760 mm Hg times the mole fraction of zinc in the liquid, $x_{Zn(l)}$, and the partial pressure of lead in

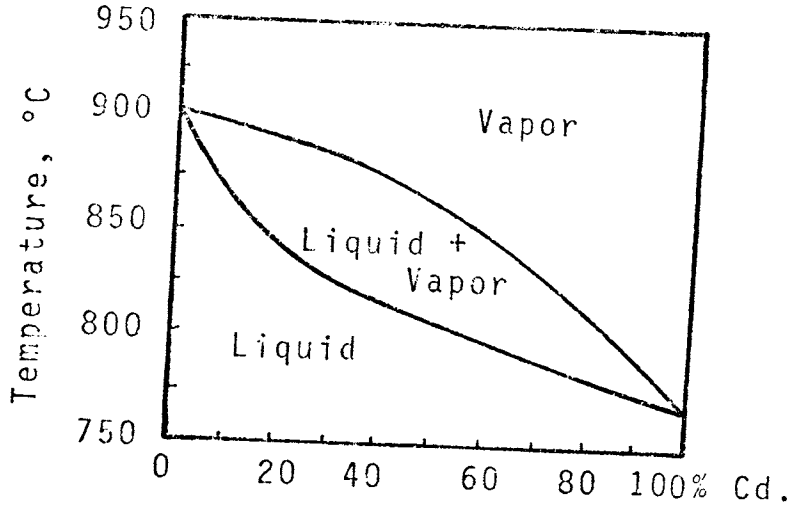

Figure 1. The Cadmium-Zinc Equilibrium Diagram at One Atmosphere Pressure(3).

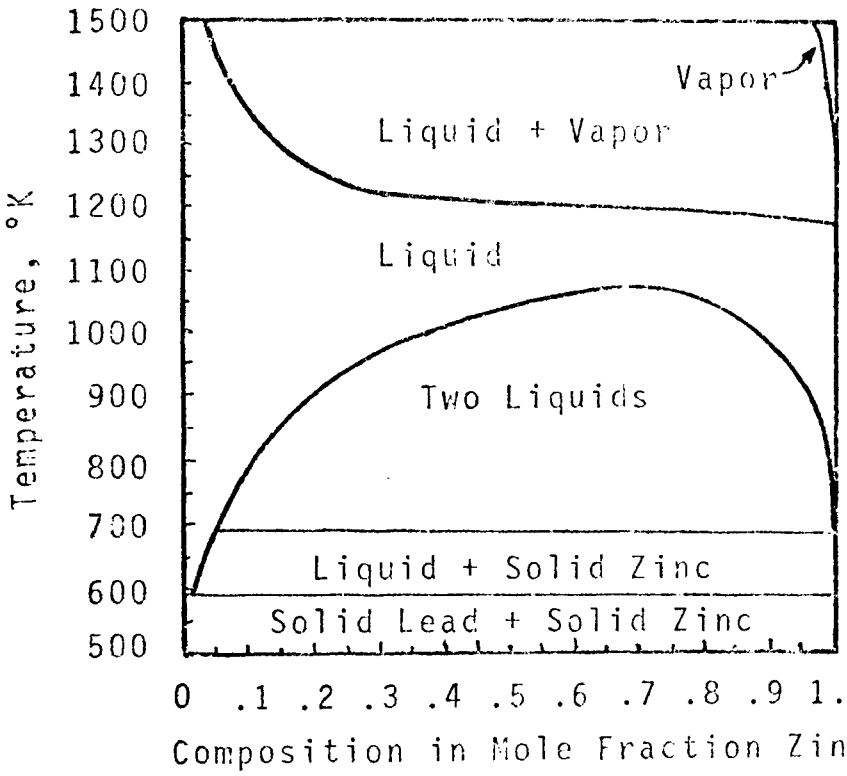

Figure 2. The Lead-Zinc Phase Diagram At One Atmosphere Pressure[4].

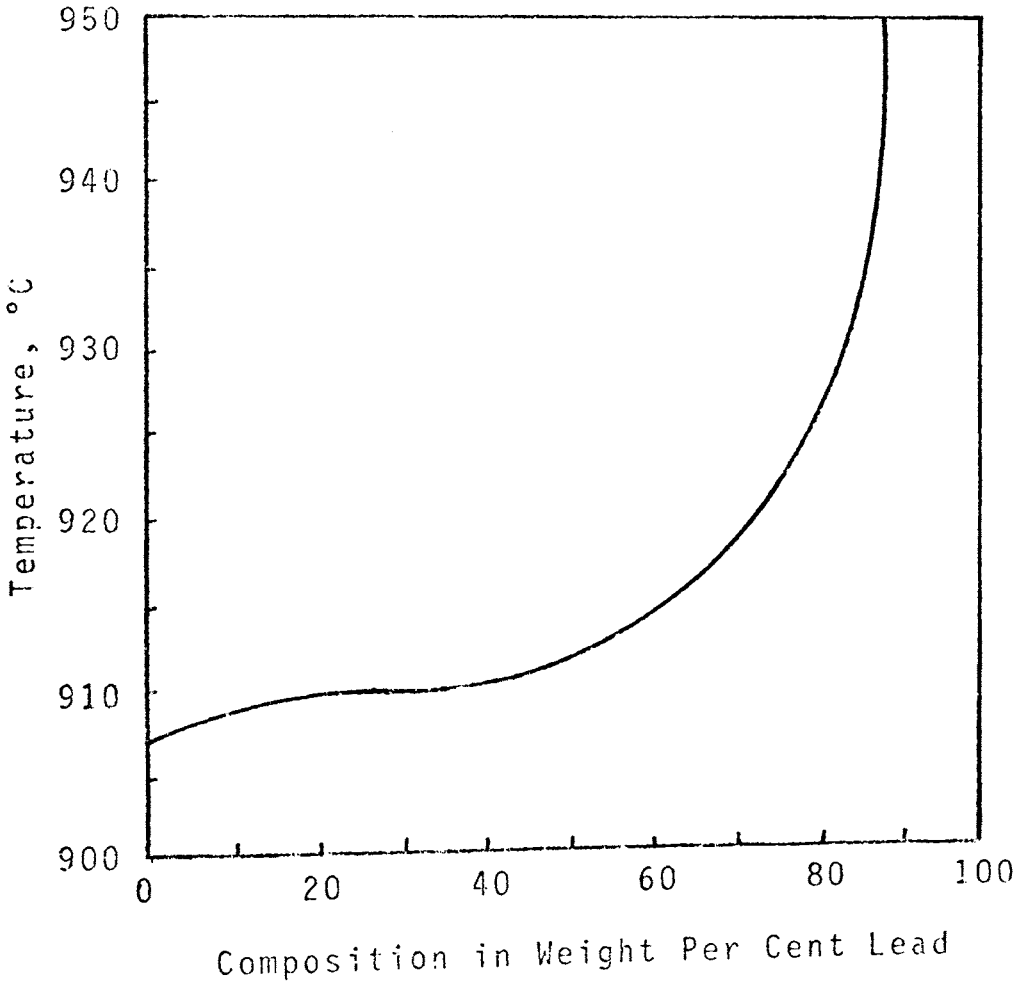

Figure 3. The Boiling Points of Zinc-Lead Alloys[3].

the vapor, $p_{Pb(g)}$, would be 0.3 times the mole fraction of lead, $x_{Pb(l)}$. Since the mole fractions in the vapor are the same as the pressure fractions in the vapor, the mole fraction of lead in the vapor, $x_{Pb(g)}$, is

$$x_{Pb(g)} = \frac{0.3\, x_{Pb(l)}}{0.3 x_{Pb(l)} + 760\, x_{Zn(l)}}$$

Therefore

$$\frac{x_{Pb(g)}}{x_{Pb(l)}} = \frac{0.3}{0.3\, x_{Pb(l)} + 760\, x_{Zn(l)}}$$

For dilute solutions of lead in zinc, $x_{Pb(l)}$ is small and $x_{Zn(l)}$ is approximately unity. Thus,

$$\frac{x_{Pb(g)}}{x_{Pb(l)}} \simeq \frac{0.3}{760} \simeq 0.0004$$

The actual ratio obtained under equilibrium conditions is only 0.004 because the activity coefficient of lead in zinc at 907°C is about 10.

Lumsden[4] gives the data in Figure 4 which shows the lead content of the vapor phase resulting from liquid zinc-lead alloys at their boiling points. The slope of this curve approaches 0.0041 as a limit as the lead content of the liquid approaches zero.

Richardson[5] claimed that by distilling and refluxing zinc at reasonable speeds under industrial conditions it is possible to produce zinc containing less than 0.001 per cent by weight of lead from a metal containing 0.01 per cent by weight of lead. Since the ratio of mole fractions is approximately equal to the ratio of weight per cents for

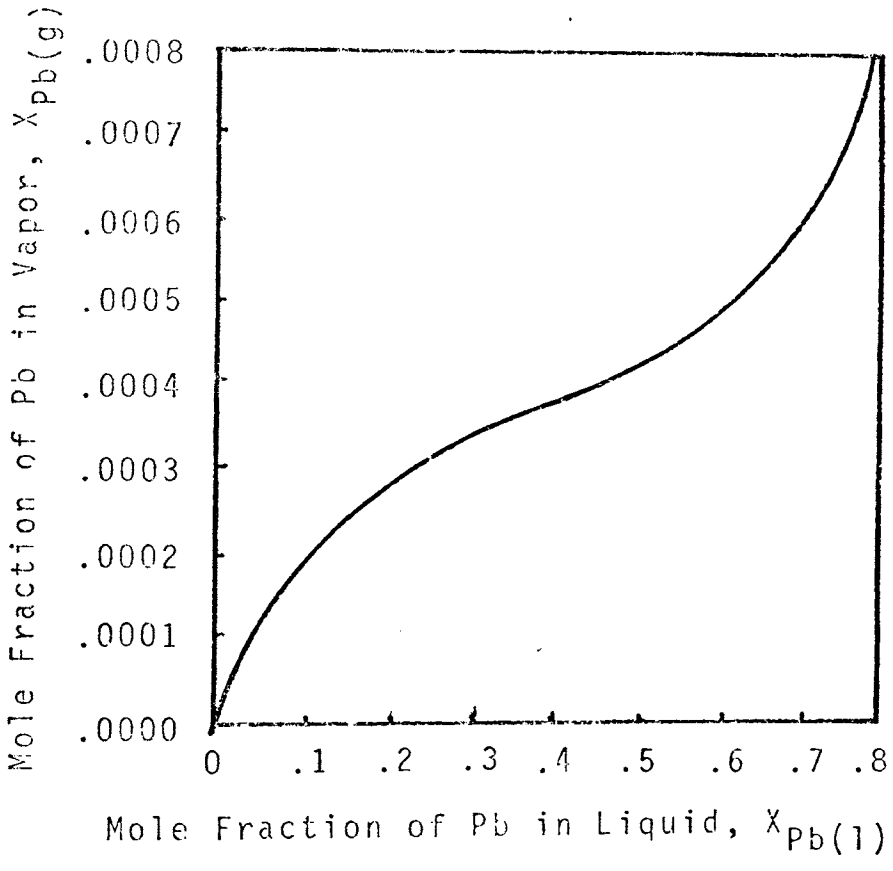

Figure 4 Composition of the Vapor in Equilibrium with Boiling Lead-Zinc Alloys[4].

dilute solutions, these weight percentages are equivalent to a mole fraction ratio of $x_{Pb(g)}/x_{Pb(1)}$, equal to approximately 0.01. These data indicate the lead content of the distilled zinc may be two and one half times greater than the equilibrium data indicate it should be.

Robson[3] also gives data on the purification attainable by distilling zinc-alloys. Robson claims that a liquid alloy containing 0.75 per cent lead will yield a vapor of 0.0030 per cent lead which corresponds to a mole fraction ratio of 0.004, very close to the theoretical value.

Robson points out that the lead content of the vapor can be unduly high in a commercial distillation process because liquid droplets form by bumping and splashing. At one time these droplets were filtered out of the vapor phase in commercial processes by passing the vapor through a coke plug or over trays containing coke or broken refractory material. This process of filtering out entrained liquid droplets did not always produce vapor of the same purity because it is possible for the droplets to come in contact with the refractory surfaces above the liquid level in the chamber where boiling takes place. Since the refractory surfaces can be very much hotter than the liquid, the droplets can be completely vaporized. Once vaporized, the lead can pass through the coke refractory filter.

From the kinetic theory of gases, the rate at which molecules of a vapor leave the surface of a liquid is given by the effusion formula

$$w = p\ (M/2\pi RT)^{\frac{1}{2}} \qquad (1)$$

where w is the rate of evaporation in grams per square centimeter per second,

p is the vapor pressure of the liquid at temperature T in dynes per square centimeter,

M is the molecular weight of the liquid in grams,

R is the gas constant in ergs per mole per degree Kelvin, and

T is the absolute Kelvin temperature.

For zinc this can be reduced to

$$w_o = 28.30\ p_o/T^{\frac{1}{2}} \qquad (2)$$

where w_o is now expressed in grams per square centimeter per minute and p_o in mm Hg. Equation (2) gives the maximum rate of evaporation of zinc at the temperature T. This evaporation rate would be obtained if a perfect vacuum could be maintained over the liquid zinc. When zinc evaporates into a perfect vacuum all of the atoms leaving the liquid phase escape, that is, none of the zinc vapor returns to the liquid phase. The derivation of the effusion formula, Equation (2), is given in Appendix 1.

The measurements of the vapor pressure of zinc by various investigators have been compiled and evaluated by Kelly[9]. He considers the vapor pressure of molten zinc to be expressed best by the following equation

$$\log p_o = -6754.5/T - 1.318 \log T - (0.0601)(10^{-3})\ T + 12.723 \qquad (3)$$

where p_o is expressed in mm Hg and T is in degrees Kelvin.

Figure 5 is taken from St. Clair and Spendlove[7] and shows the vapor pressure from the melting point up to 600°C as calculated from Equation (3). The maximum rate of evaporation, as calculated by

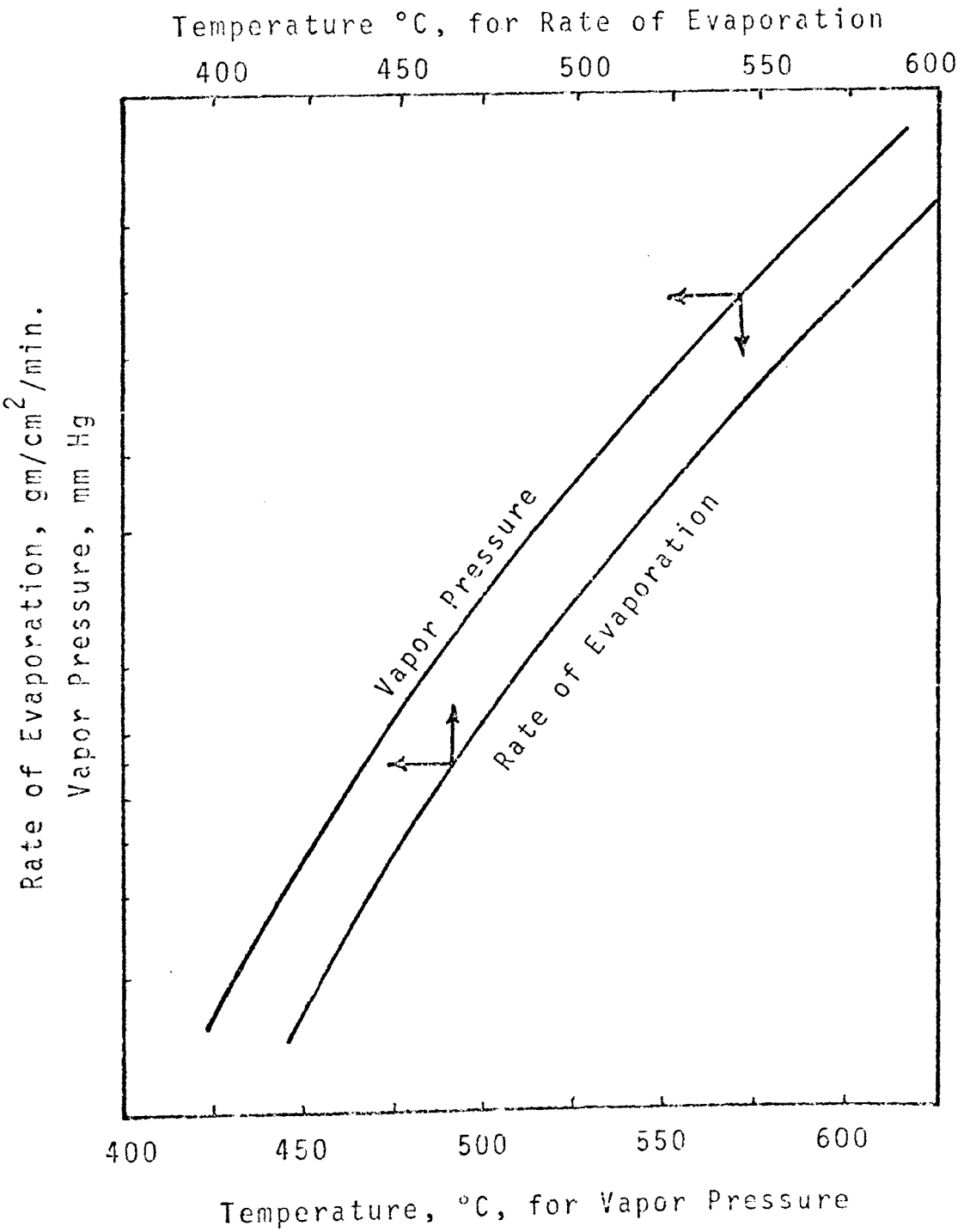

Figure 5. Vapor Pressure and Rate of Evaporation of Zinc at Various Temperatures[7].

Equation (2), is shown on the same graph. The maximum rate of evaporation at the melting point, 419°C, is only 0.140 grams per square centimeter per minute at 500°C and more than 10 grams per square centimeter per minute at 600°C.

St. Clair and Spendlove[6][7] determined the rate of evaporation at various reduced pressures and found that for a fixed power input the rate of evaporation decreased as pressure increased. In these experiments, the pressure of a residual gas, measured at a point in the system remote from liquid zinc, was reported as the pressure. The nature of the residual gas was not stated. At a low pressure of 100 microns, the observed rate of evaporation was 83 per cent of the maximum value calculated by Equation (2). At a pressure of 2000 microns the rate was only 7 per cent of the maximum value.

St. Clair and Spendlove recognized that Equation (2) only applied to the evaporation of zinc into a perfect vacuum and that the effusion formula could be used to calculate the rate of condensation of zinc if p_o in Equation (2) were replaced by the partial pressure of the zinc vapor.

$$w' = 28.30\ p_r/T^{\frac{1}{2}} \qquad (4)$$

where w' is the weight of zinc condensed, in grams per square centimeter per minute, and p_r is the partial pressure of the zinc vapor, in mm Hg.

The net rate of evaporation, w_n, when zinc is present is the difference between the maximum rate of evaporation, w_o, and the rate of condensation, w',

$$w_n = 28.30(p_o - p_r)/T^{\frac{1}{2}} \qquad (5)$$

where w_n, the net rate of evaporation, is given in grams of zinc evaporated per square centimeter of liquid surface per minute.

While St. Clair and Spendlove gave Equation (5), they did not use it to calculate the rate of evaporation. This equation is not applicable to their experiments because the gas phase was never pure zinc vapor. A residual gas of some kind was always present.

Epstein[10] has derived an equation giving the rate of evaporation of a metal from a liquid bath when a residual gas is present

$$\frac{w_1}{w_A} = \frac{2.736T}{\lambda P}(1/b)^{2/3}\left[\frac{(1 + M_A/M_B)^{\frac{1}{2}}}{1 + (\rho_B/\rho_A)^{1/3}}\right]^2 \qquad (6)$$

where w_1 is the Epstein rate of evaporation of the metal A, gm/cm^2-min, into a gaseous atmosphere, containing the metal A, and a residual gas B,

w_A is the rate of evaporation of a metal A, gm/cm^2-min, into a perfect vacuum, the maximum rate of evaporation,

T is absolute Kelvin temperature,

P is the total pressure, dynes/cm^2,

λ is the distance between the evaporating and condensing surfaces, cm,

M_A is the molecular weight of the metal A, gm,

M_B is the molecular weight of the residual gas B, gm,

ρ_A is the density of the metal A, gm/cm^3,

ρ_B is the density of the residual gas, B, gm/cm^3, and

b is the van der Waals' constant for the residual gas.

Unfortunately the Epstein equation is reported as a private communication and its derivation is not really known. The correctness of this equation is doubtful. It was claimed that the calculated rate of evaporation can be in error by a factor of 100. St. Clair and Spendlove apparently did not use it in their work.

Luchak and Langstroth[11][12] have derived an equation giving the rate of evaporation of a substance from a liquid surface when air is present (assuming no oxidation on the liquid surface).

$$w_2 = (9.60)(10)^{-4}(p)(M_A D/T\lambda) \qquad (7)$$

where

w_2 is the Luchak rate of evaporation of the metal A, in gm/cm^2-min, in gaseous atmosphere,

p is the vapor pressure of liquid at temperature T, in mm Hg,

M_A is the gram molecular weight of the metal A being evaporated,

D is the diffusivity in the gas, in cm^2/sec,

T is the temperature, in °K, and

λ is the distance between the evaporating and condensing surfaces, in cm.

Diffusivity, D, may be calculated from the following Equation (13) which has been derived by Maxwell from the kinetic theory of gases

$$D = \frac{kT^{2/3}}{P(V_A^{1/3} + V_B^{1/3})^2}\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{\frac{1}{2}} \qquad (8)$$

where

k is a constant, ranging from 0.0038 to 0.0047[13],

D is the diffusivity in the gas, cm^2/sec,

M_A is the gram molecular weight of metal A,

M_B is the gram molecular weight of residual gas B,

P is the total pressure, in atm,

T is the Kelvin temperature,

V_A is the molal volume of the metal A in liquid state at its normal boiling point, in $cm^3/g\text{-mole}$,

V_B is the molal volume of the residual gas B in liquid state at its normal boiling point, in $cm^3/g\text{-mole}$.

According to the Maxwell-Stefan[14] law of molecular diffusion, the rate of diffusion of metal A through a stagnant gas B is given as follows:

$$w_3 = \frac{(60)(P)(D)(p_{A1} - p_{A2})(M_A)}{(\lambda)(R)(T_{A1})(p_{BM})} \qquad (9)$$

where

w_3 is the Maxwell rate of diffusion of metal A in a stagnant gas, in $gm/cm^2\text{-min}$,

P is the total pressure, in atm,

D is the diffusivity of metal A in residual gas B, in cm^2/sec,

p_{A1} is the partial pressure of the metal A at the evaporating surface for a given temperature T_{A1}, in atm,

p_{A2} is the partial pressure of the metal A at the condensing surface for a given temperature T_{A2}, in atm,

M_A is the gram molecular weight of metal A,

λ is the distance between the evaporating and condensing surfaces, in cm,

R is the gas constant, 82.00 (atm)(cm)^3/(mole)(T),

T_{A1} is the absolute temperature of the metal A at the evaporating surface, in degree Kelvin,

T_{A2} is the absolute temperature of metal A at the condensing surface, in degree Kelvin,

P_{BM} is the log mean partial pressure of residual gas B, that is, $(p_{B2} - p_{B1})/\ln (p_{B2} / p_{B1})$ where p_{B1} is the partial pressure of residual gas B at the evaporating surface, and p_{B2} is the partial pressure of residual gas B at the condensing surface, in atm.

III. EXPERIMENTAL

A. Apparatus:

Four pieces of equipment were used in this investigation: (1) an electrically heated resistance furnace, (2) a condenser system, (3) a boiler, and (4) a gas atmosphere system.

An electrically heated tube furnace was used to heat a high temperature McDanel Zirco (zirconium oxide) tube which was twenty-eight inches long and had an internal diameter of two and a quarter inches. The Zirco tube was supported by two steel rings which stood in front of the furnace. The furnace was mounted on wheels to allow it to be moved back and forth over the closed end of the Zirco tube. The heated portion of the furnace consisted of Kanthal resistance wire wound on an alumina core. The wire was coated with alundum cement. An alumina sleeve covered the entire core, This heating assembly was insulated by fire bricks. The fire bricks and heating assembly were contained in a cylindrical steel shell.

The temperature of the furnace was controlled by a Wheelco controller and a platinum-platinum 10 per cent rhodium thermocouple. This thermocouple was outside the Zirco tube and allowed the temperatures to be controlled within $\pm$ 5°C.

The boiler, condenser and other details of the apparatus are shown in Figure 6. A chromel-alumel thermocouple which was attached to the condenser tube and inserted into the base of the boiler during each run was used to indicate the temperature of the molten bath. In order to prevent the hot junction of the thermocouple from alloying with zinc

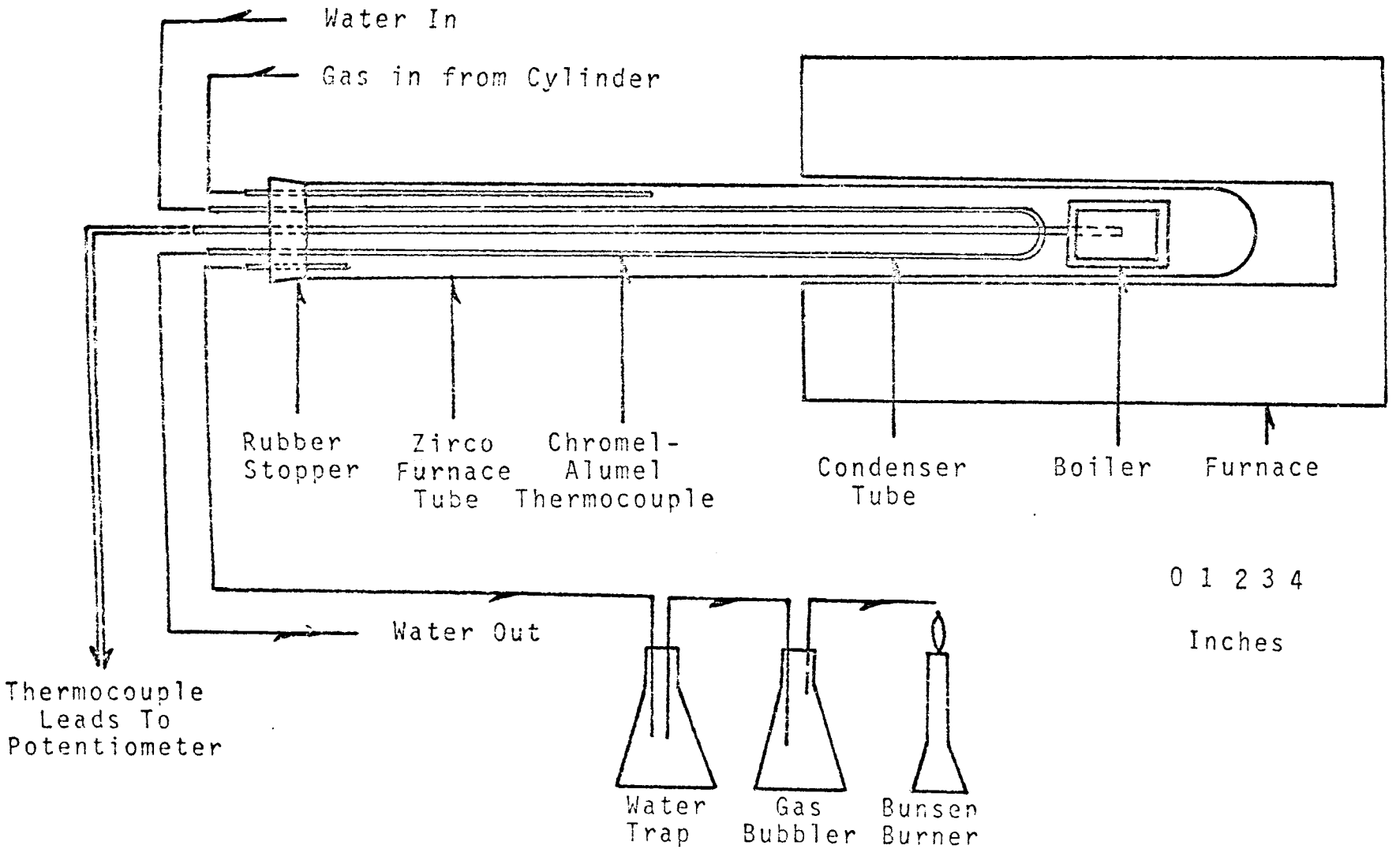

Figure 6. General Layout of Apparatus

vapor, a mullite protection tube which was thirty inches long and had a quarter inch internal diameter was used as a protection tube. Several comparisons were made between the temperature indicated by the 2 different thermocouples. In the temperature range of 700° to 900°C, it was found that the temperature of the boiler, on the average, was 20°C lower than the temperature indicated by the control thermocouple on the outside of the tube.

Figure 7 shows typical heating and cooling curves for the boiler. In an argon atmosphere the time was essentially constant for heating to a given temperature. From run to run for a given temperature the variation of heating time was less than 5 minutes. The heating time depended on the temperature used for the experiment and, as indicated by Figure 7, was in the range of 1 1/2 to 3 hours for heating to temperatures in the range 650-850°C.

The water-cooled condenser, Figure 8, was made of 3/16 inch copper tubing which was sixty inches long and U-shaped. Both ends of the condenser were placed through holes in the rubber stopper. The legs of the U-shaped condenser were held apart by a piece of copper plate. An iron ring supported the condenser and kept it centrally located inside the Zirco tube.

The boiler was made of graphite. Its basin for containing the molten zinc was 4 inches long, 1 3/8 inches wide and 5/8 inches deep. The thermocouple well was located directly beneath the metal bath. The construction of the boiler is shown in Figure 8.

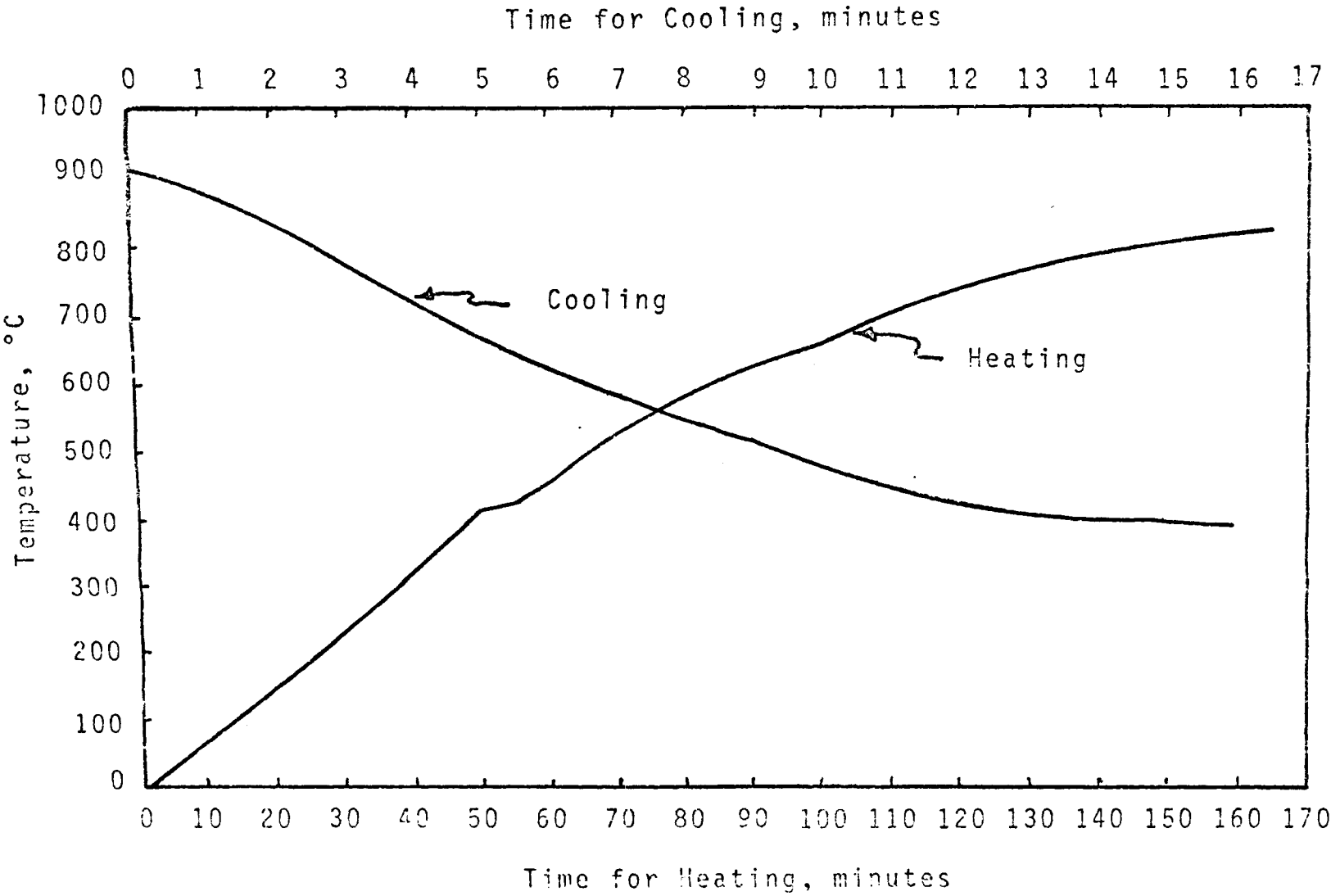

Figure 7 Heating and Cooling Rate Curve of Boiler with Zinc in Furnace

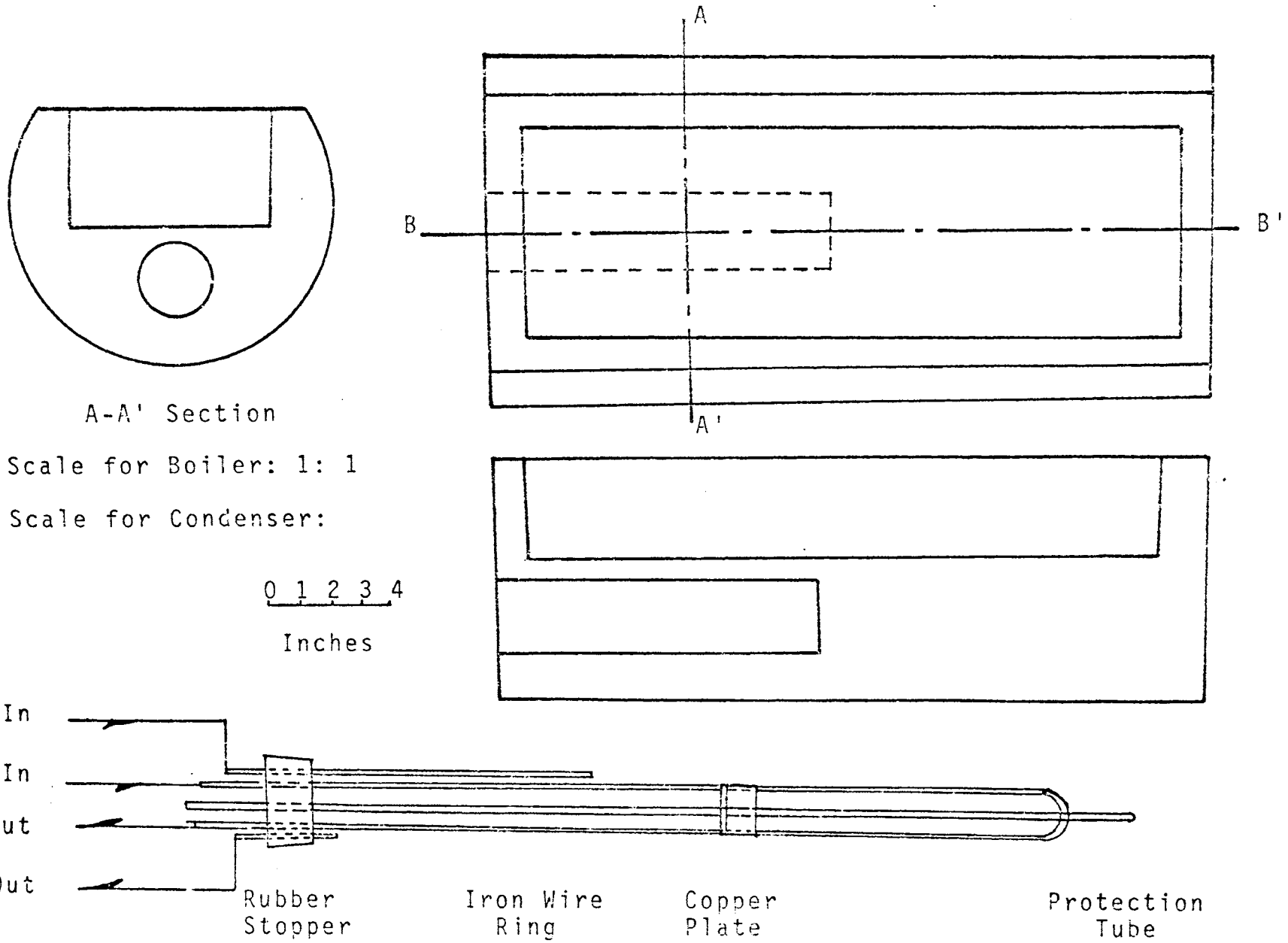

Figure 8. Construction of Boiler and Condenser

Hydrogen, carbon monoxide, argon, argon-0.1 per cent oxygen, argon-1.0 per cent oxygen and air were used as residual gas atmospheres. These atmospheres, except for the air, were obtained from gas cylinders. Air was taken from a compressed air line. The gas flow was controlled by a regulator on the gas cylinder. The gas entered the system through a copper tube which was inserted into one hole in the rubber stopper of the Zirco tube and it left through another copper tube in another hole in the stopper, Figure 8. The gas-in tube extended 11 inches into the Zirco tube while the gas-out tube extended only 3 inches into the Zirco tube.

After leaving the furnace, the atmosphere passed through a 500-ml flask which served as a trap to avoid water backing into the Zirco tube and then through another 500-ml flask which served as a gas bubbler and was used to indicate the rate of gas flow. A Bunsen burner at the end of gas train was used to ignite the hydrogen or carbon monoxide when they were used. The argon-oxygen mixtures were expelled without the burner.

B. Procedure:

The following procedure was used for the determination of the rate of evaporation for zinc at various temperatures below its boiling point. Evaporation was studied in atmospheres of argon, carbon monoxide, hydrogen, argon-oxygen mixtures and air with the total pressure approximately one atmosphere.

Ingots of special high grade zinc, assaying 0.0002 per cent iron, 0.0019 per cent lead, 0.0017 per cent cadmium, were cut into small pieces.

The weight of the sample was between 230 and 250 grams. This sample size filled the basin of the boiler to a depth of approximately 3/8 inches. The bath was 4 inches long and 1 3/8 inches wide. These dimensions were equivalent to a liquid evaporation surface of 35 square centimeters. Before placing the zinc in the boiler it was ground free of oxide.

The sample, boiler, and condenser assembly were weighed individually before each run. The sensitivity of the balance was 0.1 gram.

Before each run the position of the boiler relative to the condenser was carefully adjusted to a distance of 2.0 centimeters which was measured from the condenser tube end to the nearest end of the boiler. Care was also taken to keep the boiler horizontal. If this were not done the zinc would flow to one side of the boiler and not completely cover the bottom of the basin. If the boiler were not horizontal the evaporation surface area would not be the anticipated 35 square centimeters. In order to keep the boiler horizontal, care was also taken to prevent the rotation of the condenser while fitting the stopper into the tube. After the stopper was fitted tightly, Nu glue was applied as a sealant. Water was then passed through the condenser at a rate of 25 milliliters per second.

The gas-in tube was connected to the gas cylinder and the gas-out tube was connected to the trap and bubbler flask. The flow rate of the gas was adjusted to give a flow rate of about 10 milliliters per minute.

Before starting an experiment the equipment was cleaned of zinc from the previous experiment. Usually the condenser tube and the boiler were easily cleaned. Brushing was sufficient to clean these parts of the system. Sometimes the zinc condensed on the inside of the Zirco tube

and on the thermocouple protection tube could not be scraped off. It was necessary to heat these parts of the system in the air to oxidize the zinc and then the oxide could be brushed off easily.

After the system was cleaned, the zinc was weighed and placed in the boiler. The boiler and condenser were placed inside the Zirco tube and the system closed and sealed as indicated above. The residual gas for the particular experiment to be performed was then passed through the system for at least ½ hour before heating in order to flush out the air.

The temperature of the boiler was measured periodically during heating by using the chromel-alumel thermocouple in the bottom of the boiler. The controller was set to stop the heating when the boiler reached the desired temperature. Zero time for an experiment was the time at which the boiler reached the temperature for that experiment. After the desired time at that temperature the furnace was rolled back from the Zirco furnace tube. The tube was allowed to cool in the still air. Atmosphere and condenser water flow were maintained until the tube cooled almost to room temperature.

After the furnace tube had cooled it was opened and the condenser and boiler were removed. The residual zinc in the boiler, collected condensate and condenser assembly were weighed individually.

For each temperature and atmosphere studied a blank run was made to determine how much evaporation occurred during heating. In a blank run the furnace was rolled back from the Zirco tube as soon as the proper

temperature was reached. Other details of the procedure were as nearly as possible the same as those of a normal run.

The loss in weight of the zinc in the boiler, determined by the difference in weight of zinc added at the start of the run and the weight of the residual zinc at the end of the run, was used as the weight of zinc evaporated. The weight of condensate collected was less than the loss of weight of the zinc in the boiler. The difference in the weight of condensate and the weight of zinc evaporated varied from 0.0 to 3.5 grams.

In the experiment on evaporation of zinc from the zinc-aluminum alloys, a small piece of pure aluminum (99.99 per cent), with weight equivalent to 0.1 per cent of the total initial weight of metal in the boiler, was placed beneath the zinc at the beginning of the experiment. Except for this aluminum addition to the boiler the procedure was exactly the same as for the zinc experiment.

IV. RESULTS

A series of evaporation experiments was made to determine the rate of evaporation of zinc at various temperatures ranging from 650°C to 850°C. The results are shown in Table I. In this series of tests and in all others made during the investigation, the total pressure in the system was approximately one atmosphere. The bubbler at the end of the gas train kept the pressure slightly above barometric pressure.

In Table I, the third column gives the total weight evaporated during the test. This was the loss in weight of the zinc from the boiler. In order to obtain the amount evaporated at the temperature being studied it was necessary to substract the amount evaporated during heating to the test temperature from the total zinc evaporated.

The amount evaporated during heating was determined by blank runs at each temperature studied and is given in Table I. The first test given for each temperature is a blank run in which the system was merely heated to temperature and cooled immediately. It can be seen in Table I that the amount evaporated during heating increased in a regular manner; it increased as the test temperature increased. It can also be seen that the weight evaporated during heating became increasingly more significant as the temperature increased. At 650°C the weight loss during heating was nil while it approached approximately 50 per cent of the total weight loss for a 30 minute run at 800°C and 850°C.

The reproducibility of the data can be judged by examining the data from the duplicate 240 minute runs at 700°C and four 30 minute runs at 850°C. The maximum deviation from the average evaporation rate at

Table I: Observed Rates of Evaporation of Zinc at Various Temperatures under One Atmosphere of Argon

Test No.	Boiler Temperature, °C	Weight Evaporated, Grams	Weight of Condensate, Grams	Evaporation Time, Minutes		Evaporation Rate, Gm/Cm^2-Min
Q16	650	0	0	0		
Q 6	650	2.0	1.6	120		0.000476
Q10	650	4.0	3.3	240		0.000476
					avg.	0.000476
Q 5	700	0.2	0.2	0		
Q 2	700	5.0	2.8	120		0.00114
Q 9	700	9.6	8.5	240		0.00112
Q13	700	9.2	8.2	240		0.00107
					avg.	0.00111
Q 3	750	1.7	1.0	0		
Q14	750	7.5	4.0	75		0.00221
Q12	750	11.6	8.8	120		0.00236
					avg.	0.00229
Q 7	800	4.0	3.5	0		
Q15	800	8.5	5.5	30		0.00429
Q11	800	13.5	11.0	60		0.00452
					avg.	0.00441
K 3	850	6.0	6.0	0		
K 1	850	14.9	13.1	30		0.00829
K 2	850	15.3	13.5	30		0.00886
K 4	850	15.0	13.3	30		0.00856
K 5	850	15.0	13.0	30		0.00858
					avg.	0.00858

850°C was 3.38 per cent while it was 3.60 per cent at 700°C. Table II shows the average evaporation rate in argon at each temperature studied. The maximum deviation from the average evaporation rate in this whole series of tests was 3.60 per cent in one of the 700°C experiments.

The fourth column in Table I gives the weight of zinc condensed. This was the zinc that could be removed from the condenser tube and the inside surfaces of the system after each run. This was always less (except in some experiments in which the atmosphere was oxidizing as mentioned below) than the loss in weight of zinc from the boiler because it was not possible to collect and weigh all the zinc evaporated. Some of the zinc apparently condensed as a liquid phase on the hot surfaces. After cooling, this zinc could not be removed and weighed. This zinc had to be oxidized to remove it from the system. The amount of condensate weighed was less than the amount of zinc evaporated. The difference in these two figures, shown in columns three and four of Table I, was found between 0.0 and 3.5 grams.

The evaporation time was varied and it was found that the evaporation rate was independent of time in the range of time studied. At the lower temperatures the time had to be relatively long in order to obtain sufficient evaporation to permit weighing. On the other hand, it was considered desirable to limit the time at the higher temperatures because the larger amount of condensate at the higher temperatures tended to fill up the inside of the tube. The condensate was not a dense mass of zinc.

The evaporation rate given in the last column of Table I was calculated by subtracting the amount of zinc evaporated during heating from the

Table II: Average Evaporation Rates in Argon and Maximum Deviations from Average Rates

Boiler Temperature, °C	Average Evaporation Rate, Gm/Cm^2-Min	Maximum Deviation, Per Cent
650	0.000476	0
700	0.00111	3.60
750	0.00229	3.49
800	0.00441	2.72
850	0.00858	3.38

total amount evaporated in the test and dividing this difference by the product of the time and the surface area of the liquid zinc in the boiler.

The area of evaporation was taken to be the top surface area of the basin in the boiler, which was 35.0 square centimeters. Care was taken to have the boiler horizontal in each experiment. At the end of each experiment the appearance of the solidified zinc in the boiler indicated whether or not it covered the bottom of the boiler completely and presented the proper evaporation surface. The weight of the boiler remained constant during the investigation. This was taken as an indication that the boiler did not oxidize and that the basin remained the same size from one experiment to the next.

The rate of evaporation in argon was found to vary in a regular manner with temperature. The rate was found to increase slowly at lower temperatures and rapidly at higher temperatures as shown in Figure 9.

In another series of experiments the effect of gas atmosphere on the rate of evaporation of zinc was determined. The results of these tests are shown in Table III. These experiments were all conducted at barometric pressure and 750°C. Some of the atmospheres were reducing while others were oxidizing.

The rate of evaporation in hydrogen at 750°C, 0.00456 gm/cm^2-min, was approximately twice the 0.00229 gm/cm^2-min rate in argon. The evaporation rate in the argon-oxygen atmospheres was apparently independent of the oxygen concentration of the mixtures studied even though the oxygen concentration varied by a factor of ten. However, the oxygen present

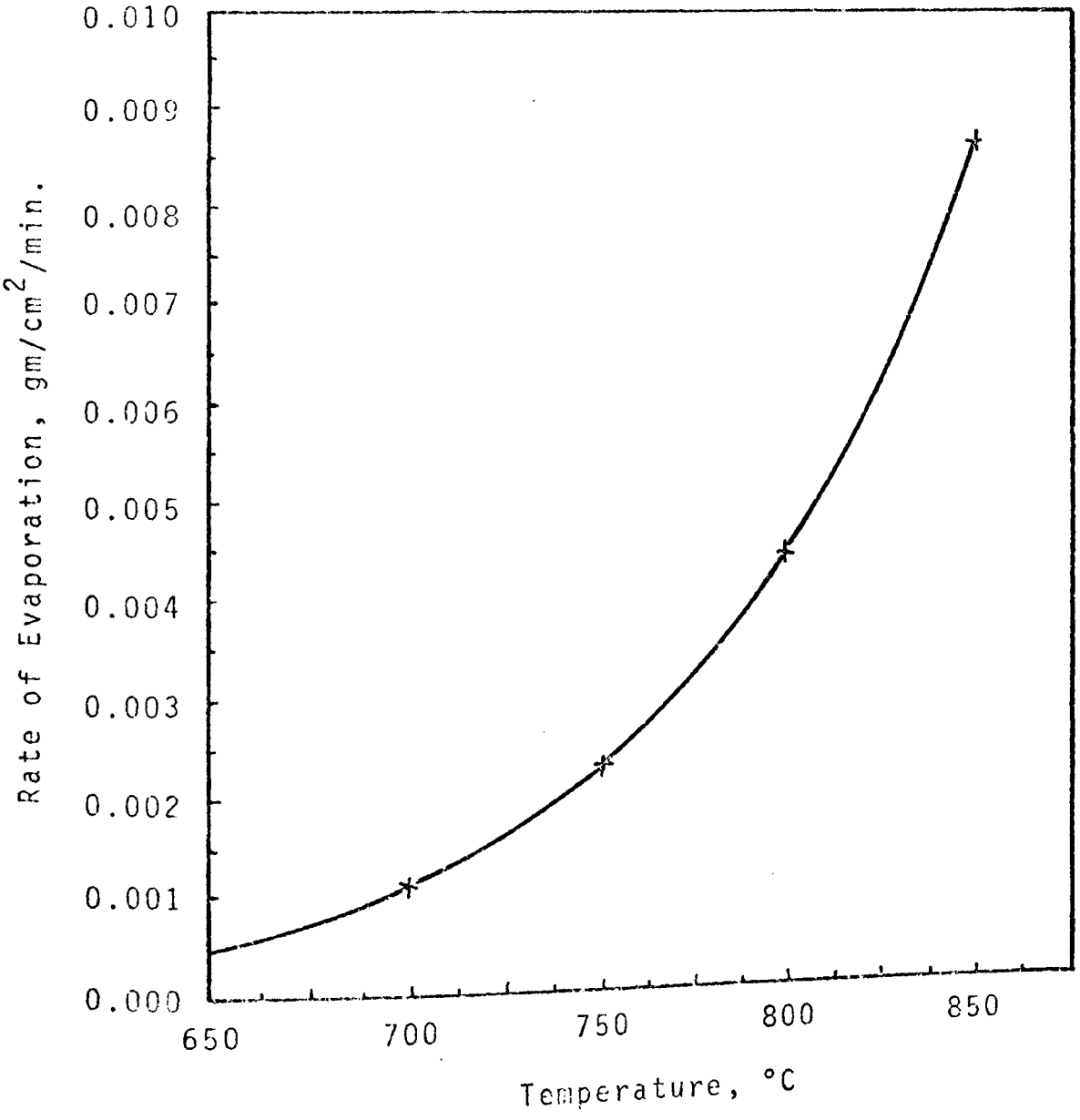

Figure 9 Observed Rate of Evaporation of Zinc in Argon at One Atmosphere Pressure

Table III: Rate of Evaporation of Zinc in Various Atmospheres at 750°C.

Test No.	Weight Evaporated, Grams	Weight of Condensate, Grams	Evaporation Time, Minutes		Evaporation Rate, Gm/Cm^2-Min
		Hydrogen			
N 5	5.3	5.0	0		
N 4	10.5	9.5	30		0.00456
		Argon-0.1% Oxygen			
R 2	1.4	1.5	0		
R 5	4.6	4.6	60		0.00153
R 1	6.3	6.7	99		0.00142
R 7	8.3	7.5	120		0.00164
R 3	11.1	9.0	180		0.00154
R 4	14.8	14.2	240		0.00160
				avg.	0.00155
		Argon-1.0 Oxygen			
S 1	1.1	1.1	0		
S 2A	7.2	6.2	120		0.00145
S 2B	7.2	7.6	120		0.00145
S 8	7.8	7.0	120		0.00160
S 6	11.2	11.2	180		0.00160
S 7	14.6	15.1	240		0.00161
S 5	21.5	18.3	360		0.00162
				avg.	0.00157
		Air			
V 1	0.3	0	120		0.00007
		Argon			
Q 3	1.7	1.0	0		
Q14	7.5	4.0	75		0.00221
Q12	11.6	8.8	120		0.00236
				avg.	0.00229

in the mixtures caused the evaporation rate to be lower than that in pure argon. The evaporation rate in air appeared to be almost zero.

When the argon-oxygen mixtures were used the difference between the weight of zinc evaporated and the weight of the condensate tended to be less than when pure argon or reducing atmospheres were used. In several instances, tests R 2, S 2B and S 7, the weight of the condensate was actually more than the amount evaporated. In these experiments the condensate contained zinc oxide. The appearance and physical nature of the condensate was markedly different in the argon-oxygen atmosphere.

It should be noted that the surface on the solidified zinc in the boiler after the argon-0.1% oxygen experiments was relatively clean. A slight discoloration or dullness was observed on the surface of the zinc toward the condenser end of the boiler while the surface furthest from the condenser had a bright and metallic appearance. The surfaces of the solidified zinc from argon-1.0% oxygen experiments were entirely discolored. The surface on the zinc in the boiler after experiments in air was thoroughly oxidized.

A carbon monoxide atmosphere was used at 850°C. These experiments are reported in Table IV. The rate of evaporation in carbon monoxide was almost identical to that in argon.

The final series of experiments determined the rate of evaporation of zinc at 750°C from a zinc-aluminum alloy containing 0.1 per cent aluminum in an atmosphere of argon. Table V gives data obtained from these experiments. The evaporation rate appeared to increase with increase in time. The rate from the 60 minute run was 16 per cent less that the

0.00114 gm/cm^2-min average rate. The rate found in the 120 minute run was 17.5 per cent more than the average evaporation rate. The rate of evaporation from the alloy was approximately one half the evaporation rate determined for pure zinc.

Table IV: Rate of Evaporation of Zinc in Carbon Monoxide at 850°C.

Test No.	Weight Evaporated, Grams	Weight of Condensate, Grams	Evaporation Time, Minutes	Evaporation Rate, Gm/Cm^2-Min
L 6	6.0	6.0	0	
L 3	15.0	13.5	30	0.00858
L 4	15.5	13.5	30	0.00905
L 5	15.3	14.8	30	0.00886
			avg.	0.00883

Table V: Rate of Evaporation of Zinc-Aluminum Alloy Containing 0.1% Al in Argon at 750°C.

Test No.	Weight Evaporated, Grams	Weight of Condensate, Grams	Evaporation Time, Minutes	Evaporation Rate, Gm/Cm^2-Min
T 3	0.2	0.2	0	
T 1	2.2	2.2	60	0.000953
T 2	5.0	5.0	120	0.00114
T 4	11.5	11.0	240	0.00134
			avg.	0.00114

V. DISCUSSION

It is possible to distinguish between two vaporization processes: boiling and evaporation. Boiling is considered to be a vaporization process in which the vapor pressure of the liquid equals or exceeds the pressure of the gas phase over the liquid surface. The rate of boiling is determined by the rate of heat transfer because the latent heat of vaporization must be supplied to the boiling liquid before it can change into a vapor. The vapor is removed from the liquid surface by flow or bodily movement of the gas phase as a whole rather than by diffusion.

Evaporation is a vaporization process in which the vapor pressure of the liquid is less than the pressure of the gas phase in contact with the liquid. The rate of evaporation is not controlled by the rate of heat transfer. The evaporation rate is controlled by the rate of removal of vapor from the liquid-vapor interface region. Vapor may be removed from the vicinity of the liquid surface by diffusion of the vapor through the gas phase or the vapor may be removed from the vicinity of the liquid surface by the gas phase if the gas is flowing over the liquid surface.

In this investigation the rate of evaporation of zinc has been determined experimentally as a function of temperature in several residual gas atmospheres. These results are compared with calculated rates and are discussed below.

Three equations are available for calculation of the evaporation rate of zinc into a gas phase containing an inert or reducing residual gas. These equations, derived by Epstein, Luchak and Langstroth, and

and by Maxwell and Stefan, have been given in the literature review as equations (6), (7) and (9). Sample calculations using these equations to obtain the evaporation rate of zinc at 650°C in argon are outlined in Appendix 2. The calculated rates and the corresponding observed rates are tabulated in Table VI.

The calculated evaporation rates using the three equations were all of the same order of magnitude and can be considered to show reasonable agreement with the observed rates. With argon or carbon monoxide atmospheres all three equations give approximately the same evaporation rate at 750°C. At temperatures below 750°C the Epstein equation gives the lowest rate of evaporation and the worst agreement with the observed rate while this same equation gives the highest evaporation rate and the best agreement with the observed rate at higher temperatures. The observed rates of evaporation were higher than the calculated rates with the one exception of the evaporation rate in hydrogen using the Epstein equation.

There are a number of uncertainties in the data used to calculate the evaporation rate and these could be responsible for some of the disagreement between the calculated and the observed rates. The total pressure on the zinc was assumed to be one atmosphere for all calculations. The total pressure was actually slightly above barometric pressure during the experiments.

All three equations are based on a condenser surface parallel to the surface of the evaporating liquid. This was not the case in the present experiments. The condenser and the surface of the zinc were in approximately the same plane. The condenser was about 2.5 centimeters

Table VI: Averaged Observed Rates and Corresponding Calculated Rates of Evaporation of Zinc at Various Temperatures under One Atmosphere of Argon, Carbon Monoxide, and Hydrogen

Boiler Temperature, °C	Observed Rate, Gm/Cm^2-Min	Epstein Rate, Gm/Cm^2-Min	Luchak Rate, Gm/Cm^2-Min	Maxwell Rate, Gm/Cm^2-Min
		argon		
650	0.000476	0.000114	0.000244	0.000252
700	0.00111	0.000364	0.000505	0.000756
750	0.00229	0.00106	0.00115	0.00126
800	0.00441	0.00281	0.00214	0.00252
850	0.00858	0.00706	0.00409	0.00595
		carbon monoxide		
850	0.00883	0.00763	0.00434	0.00624
		hydrogen		
750	0.00456	0.0121	0.00418	0.00459

away from the near side of the molten zinc and about 12.5 centimeters away from the far side of the bath. The distance to the center of the bath, 7.5 centimeters, was used in the calculations but it is not certain that this is the correct distance to use. Since the calculated evaporation rate is inversely proportional to distance between condenser and evaporating liquid, if the distance to be used in the calculations should be appreciably different from 7.5 centimeters the calculated evaporation rates would be appreciably in error. For example, if the correct distance were 2.5 centimeters the calculated rates of evaporation would be larger by a factor of three while a distance of 12.5 centimeters would yield calculated values 0.6 times the values given in Table VI.

The surface temperature of the zinc in these experiments was not measured. It was assumed to be equal to the temperature measured by the thermocouple inserted in boiler below the bath. The surface temperature could have been lower than the recorded temperature. St. Clair and Spendlove[7] measured the surface temperature of the zinc in some of their experiments and found it to be about 35°C lower than the temperature in the main mass of the zinc. If the correct surface temperature of the zinc were lower than the recorded temperature a lower temperature should have been used in the calculations and this would have caused a greater difference between the calculated and the observed results. The vapor pressure of zinc would be lower at a lower temperature and this enters into the calculation with each of the three equations.

In the Epstein equation there is some doubt about the correct densities to be used. As shown in Appendix 2, it was assumed that the density of the zinc was that of zinc vapor at the temperature of the

liquid zinc and at a pressure equal to the vapor pressure of the zinc. The density of the residual gas was calculated to be the density of gas at the temperature of the zinc and at a pressure equal to its partial pressure over the zinc surface assuming the gas phase to be saturated with zinc.

Another factor that could influence the difference between the observed and calculated rates of evaporation was the flowing gas used in the present experiments. The residual gas is assumed to be stagnant in the derivation of the three equations. It is not possible to say how the flowing residual gas affected the observed evaporation rate in the experiments. Any movement of the gas phase over the liquid would tend to increase the evaporation rate. However, the residual gas entered cold and could have produced unknown temperatures variations within the system.

Consideration of the uncertainties discussed above indicates that the agreement between the observed and calculated evaporation rates is indeed good. It was stated[10] that the Epstein equation could yield rates different from the actual rate by a factor of 100. All three calculated rates agreed with each other by a factor of 2.2 or less. At the lowest temperature of 650°C the calculated evaporation rates were less than the observed rate by a factor of about two to four while at the highest temperature of 850°C the best calculated rate using the Epstein equation was approximately 85 per cent of the observed rate. The greatest difference was between the rate calculated with the Luchak-Langstroth equation and the observed rate; the Luchak-Langstroth value being low by a factor of about 2.1.

The observed and calculated rates of evaporation of zinc in argon are shown in Figure 10. The rate calculated with the Epstein equation is lowest at low temperatures and approaches the observed rate at the higher temperatures. The density ratio in the denominator of the Epstein equation is relatively large at low temperatures and decreases rather rapidly as temperature increases. This density ratio term in the Epstein equation is responsible for the more rapid rise in the Epstein evaporation rate as temperature increases.

Evaporation of liquid zinc may be pictured as a two-step process. In the first step atoms of zinc escape from the liquid phase into the space above the liquid surface. The second step involves diffusion of the zinc vapor away from the liquid surface into infinite space or to a condensing surface.

If liquid zinc evaporates into a vacuum, the rate is a maximum because every atom that crosses the liquid-vacuum interface escapes from the liquid phase. However, when a gas phase is present over the liquid surface every zinc atom that crosses the liquid-gas interface does not escape from the liquid phase in the sense that it moves out into infinite space or is captured by a condensing surface. Some of the atoms that leave the liquid phase collide with gaseous atoms or molecules and as a consequence are knocked back into the liquid phase. Furthermore, the atoms or molecules in the gas phase interfere with the movement of the zinc atoms away from the liquid, that is, they reduce the rate of diffusion of the zinc. Thus, the presence of a residual gas should slow down both steps in the evaporation process.

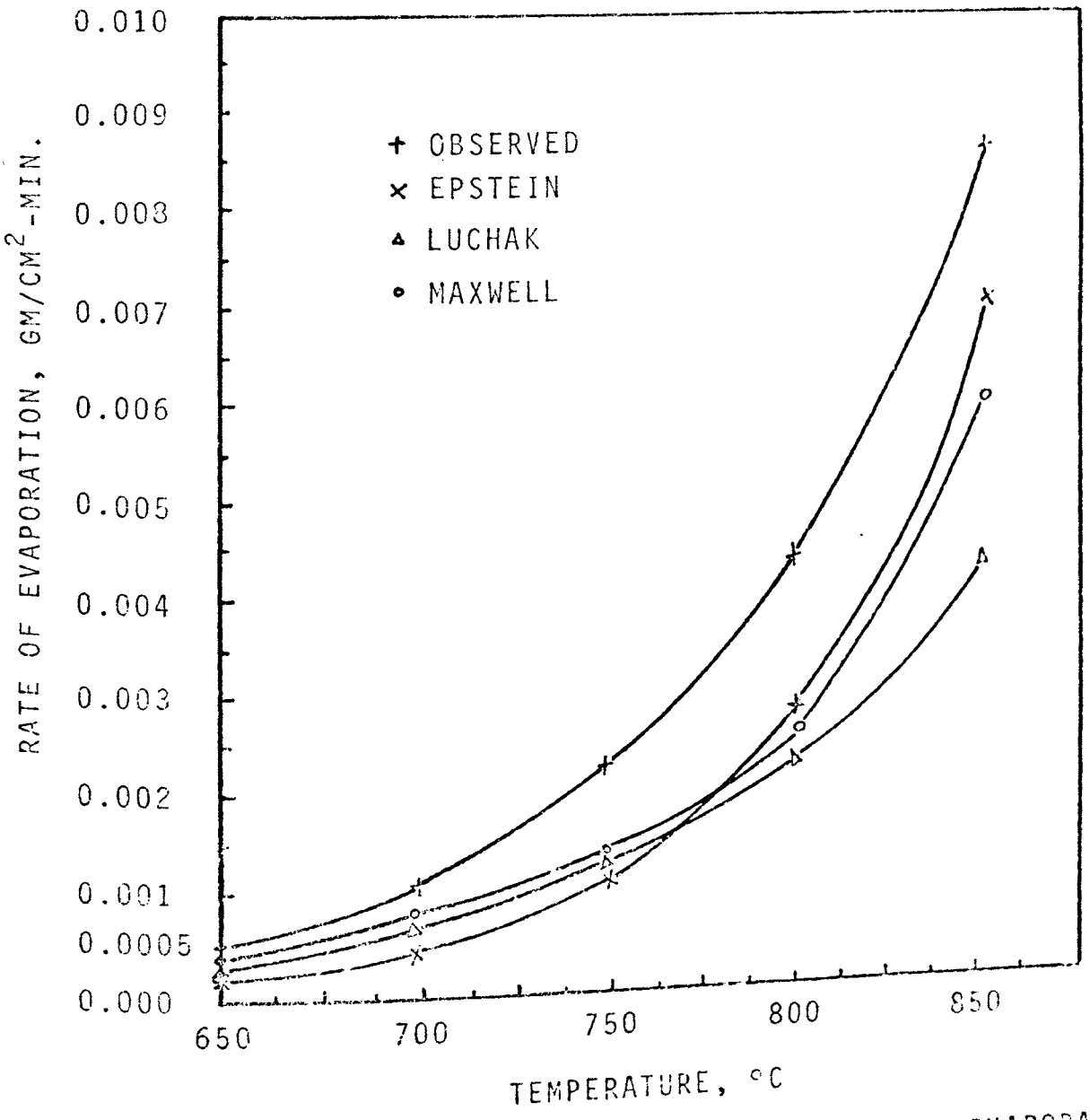

FIGURE 10. THE OBSERVED AND CALCULATED RATES OF EVAPORATION OF ZINC IN ONE ATMOSPHERE OF ARGON.

The kinetic theory of gases[8] has been used to make certain calculations which are discussed below. The results of these calculations may indicate how the two steps in the evaporation process are affected by the residual gases used in this investigation.

It is assumed that the effect of the residual gas on the net rate of escape of zinc atoms from the liquid is proportional to a force exerted by atoms or molecules in the gas phase on the zinc atoms immediately above the liquid zinc surface. The force under consideration is responsible for returning some of the zinc atoms to the liquid phase. This force is the result of the collision between the zinc atoms and molecules of residual gas. The kinetic theory of gases permits calculation of the ratio of the forces exerted by the different residual gases on the zinc atoms.

The force exerted on the zinc atoms will be proportional to the rate of change of momentum of the zinc atom as a consequence of collisions with the residual gas. A number that should be approximately proportional to the force is obtained by calculating the change of momentum in a particular kind of collision and multiplying this by the total number of collisions between zinc atoms and residual gas atoms or molecules that occur in a unit of volume per second. Both quantities of this product are calculated rather easily.

The collision for which the change of momentum of the zinc atom is most easily calculated is one in which the zinc and residual gas collide head-on and each has its root mean square velocity u which is given by

$$u = \sqrt{3RT/M} \qquad (10)$$

where

u is the root mean square velocity in cm/sec,

R is the gas constant in ergs/g.mole-°K,

T is the absolute Kelvin temperature,

M is the molecular weight in gms.

The velocities of the zinc atom and the residual gas atom or molecule after the collision can be calculated by solving the two simultaneous equations for the conservation of energy and of momentum. Thus,

$$(1/2)\, M_{Zn} u^2_{Zn} + (1/2)\, M_G u^2_G = (1/2)\, M_{Zn} u'^2_{Zn} + (1/2)\, M_G u'^2_G \qquad (11)$$

and

$$M_{Zn} u_{Zn} + M_G u_G = M_{Zn} u'_{Zn} + M_G u'_G \qquad (12)$$

where

M_{Zn} and M_G are the molecular weights of the Zn and residual gas respectively, in gms,

u_{Zn} and u'_{Zn} are velocities of the zinc before and after the collision, respectively, in cm/sec.

The change in momentum of the zinc atom in this collision will be

$$M_{Zn} u'_{Zn} - M_{Zn} u_{Zn} \qquad (13)$$

The total number of collisions in one second between all the atoms of zinc and all the atoms or molecules of residual gas in one cubic centimeter, $Z_{Zn,G}$ is given by

$$Z_{Zn,G} = (1/4) n_{Zn} n_G (\sigma_{Zn} + \sigma_G)^2 \left[8\pi RT (M_{Zn} + M_G)/M_{Zn} M_G\right]^{1/2} \qquad (14)$$

where

n_{Zn} is the number of zinc atoms per cm^3,

n_G is the number of atoms or molecules of residual gas per cm^3,

σ_{Zn} is the diameter of a Zn atom in cm,

σ_G is the diameter of the atom or molecule of residual gas, and

the other symbols are as defined above.

It is assumed that the force exerted by the residual gas on the zinc atoms is at least approximately proportional to the product, $F_{Zn,G}$, of the change in momentum in the one kind collision and the total number of collisions

$$F_{Zn,G} = Z_{Zn,G}(M_{Zn}u'_{Zn} - M_{Zn}u_{Zn}) \qquad (15)$$

The factor $F_{Zn,G}$ for argon and carbon monoxide as residual gases at 850°C and for argon and hydrogen at 750°C have been calculated. These calculations are shown in Appendix 3. The results are given below:

Residual Gas	Temperature, °C	$F_{Zn,G}$
Ar	850	2.35×10^{34}
CO	850	2.12×10^{34}
Ar	750	1.432×10^{34}
H_2	750	0.848×10^{34}

The above four force factors, $F_{Zn,G}$, can be compared to obtain the relative forces exerted by the residual gases on the zinc. The ratio of $F_{Zn,Ar} : F_{Zn,CO}$ is 1.1 : 1 and indicates that argon and carbon monoxide exert approximately the same force on the zinc atoms as they attempt to escape from the liquid zinc at 850°C. Since the argon exerts a greater force on the zinc atoms it should be easier for the zinc atoms to escape from the liquid phase when the carbon monoxide is the residual gas.

From Table I the average rate of evaporation of zinc in argon at 850°C is 0.00858 g/cm^2-min while from Table IV the rate in carbon monoxide is 0.00883. The ratio of the rate of evaporation in carbon monoxide to that in argon is 1.03 : 1. Since 1.1 is very approximately the same as 1.03 these ratios could indicate that the effect of the residual gas is to impede the escape of atoms from the liquid phase and that the evaporation rate is inversely proportional to the force exerted by the residual gas on the escaping zinc atoms.

The ratio of the force factors $F_{Zn,Ar}$: F_{Zn,H_2} at 750°C is about 1.7 : 1 and should indicate that argon exerts almost twice as much force on the escaping zinc atoms as the hydrogen. If the evaporation rate is controlled by this force and is inversely proportional to the force the ratio of the evaporation rate of zinc in hydrogen at 750°C should be a little less than twice that in argon. The evaporation rates can be obtained from Table I and III and are 0.00456 g/cm^2-sec in hydrogen and 0.00229 g/cm^2-sec in argon giving a ratio of about 2 : 1. This ratio of evaporation rates is slightly high but certainly of the correct order of magnitude.

The evaporation process was described as two steps: escape from the liquid phase and diffusion away from the liquid. The effect of the residual gas on the second step, diffusion of the zinc away from the liquid, has already been calculated by the Maxwell-Stefan equation and the results of these calculations are shown in Table VI. At 850°C the rate of diffusion of zinc in carbon monoxide to that in argon should be 0.00624 : 0.00595 or 1.05 : 1.

This ratio is essentially the same as the evaporation rate of zinc in carbon monoxide to that in argon, 1.03 : 1. This could indicate that the rate of evaporation is controlled by the diffusion rate of the zinc in the residual gas. However, since the effect of carbon monoxide and of argon on the first step in the evaporation were shown to be about the same it is not clear from the results on these two residual gases what the effect of a residual gas might be.

The calculated diffusion rates of zinc in hydrogen and in argon at 750°C give a ratio of 0.00459 : 0.00126 of about 3.6 : 1. In this case the ratio of evaporation rates is only about 2 : 1 and is closer to the inverse of the calculated ratio of the forces tending to prevent the zinc from leaving the liquid phase. While the data are limited, they tend to indicate that as a residual gas, hydrogen is more effective in returning zinc atoms to the liquid phase than it is in reducing the rate of diffusion of zinc atoms away from this liquid surface.

It is difficult to attach significance to the results obtained from the experiments on evaporation of zinc in atmospheres with free oxygen. The two argon-oxygen atmospheres, one with 0.1 per cent oxygen, and the other with 1.0 per cent oxygen reduced the evaporation rate of the zinc about the same, to approximately one half its value in pure argon. It is reasonable to expect an oxide film on the surface of the liquid zinc to interfere with the escape of zinc atoms from the liquid. However, it is not clear why both these oxygen concentrations gave the same evaporation rate.

It is possible that the evaporating zinc vapor in the argon-oxygen atmospheres reacted with the oxygen over the liquid zinc surface forming

zinc oxide and reducing the oxygen concentration to a relatively low value which was the same at the liquid zinc surface in both atmospheres. If the conditions were approximately the same at the liquid zinc surface in both atmospheres, the evaporation rate should have been the same. Another possibility to explain the same results in these two atmospheres is that the relatively thin oxide film on the liquid zinc surface was not continuous and that the degree of discontinuity was approximately the same in these atmospheres. Thus, the effective evaporation surface might have been the same in both atmospheres. On this basis it can be postulated that in the much higher oxygen concentration of air, a much thicker and almost continuous oxide layer formed on the liquid surface and this reduced the evaporation to a very low value.

The experiments with zinc-aluminum alloys were of an exploratory nature. The lower rate of evaporation was not expected. No explanation is offered for this effect of the aluminum addition. Physical examination of the tested samples did reveal that there was probably segregation of the aluminum, thus the melt was not homogeneous.

VI. CONCLUSIONS

1. The rate of evaporation of zinc is inversely proportional to some function of the pressure and directly proportional to some function of the temperature.

2. The rate of evaporation is dependent upon the physical nature of the non-oxidizing residual gas, in particular, the size and mass of its atoms or molecules.

3. The rate of evaporation is markedly decreased in an oxidizing residual gas, with the lower rates being obtained with atmospheres of higher oxygen partial pressures.

4. The experimentally determined evaporation rates agree well with those calculated from equations in the literature.

BIBLIOGRAPHY

(1) CYR, H. M. (1927) "Pure Zinc." Trans. Amer. Electrochem. Soc., 52, p. 349.

(2) PIERCE, W. M. and R. K. WARING (1936) "Process for the Refining of Zinc by Redistillation." AIME Trans., 121, p. 445-452.

(3) ROBSON, S. (1950) "Refining of Zinc." The Refining of Non-Ferrous Metals (a symposium). London, p. 335.

(4) LUMSDEN, J. (1948) "Thermodynamics of Lead-Zinc Alloys." The Physical Chemistry of Process Metallurgy. Faraday, London, p. 62.

(5) RICHARDSON, F. D. (1950) Principles of Extraction and Refining Processes. The Principles of Extraction and Refining of Metals. The Institution of Metallurgists, p. 90-93.

(6) ST. CLAIR, H. W. and M. J. SPENDLOVE (1950) "Rate of Evaporation of Zinc at Low Pressures." U. S. Bureau of Mines, R. I. 4710.

(7) ST. CLAIR, H. W. and M. J. SPENDLOVE (1951) "Rate of Evaporation of Zinc at Low Pressures." Journal of Metals, p. 1192-1197.

(8) LOEB, L. B. (1934) The Kinetic Theory of Gases. McGraw-Hill Book Company, Inc., New York.

(9) KELLY, K. K. (1935) "Contributions to the Data of Theoretical Metallurgy," U. S Bureau of Mines. Bulletin No. 383.

(10) SEYBOLT, A. U. and J. E. BURKE (1953) "Melting and Casting," Experimental Metallurgy. John Wiley and Sons, Inc., New York, p. 189-191.

(11) LUCHAK, G. and G. O. LANGSTROTH (1950) "Application of Diffusion Theory to Evaporation from Droplets and Flat Surfaces." Can. J. Res. A., 28, p. 574.

(12) BURROW, G. (1960) "Theory of Operation," Molecular Distillation. Oxford at the Claendon Press, p. 27-28.

(13) GILLAND, E. R. (1934) "Diffusion Coefficients in Gaseous Systems." Industrial and Engineering Chemistry, 26, p. 681-685.

(14) LARIAN, M. G. (1958) Mass Transfer. Fundamentals of Chemical Engineering Operation. Prentice-Hall, Inc., Englewood Cliffs, N. J., p. 169-171.

(15) GLASSTONE, S. (1946) Textbook of Physical Chemistry. 2nd ed., D. Van Nostrand Company, Inc., p. 276.

(16) LANGE (1939) Handbook of Chemistry. Handbook Publishers, Sandusky, Ohio, p. 1253-1256.

(17) ibid, p. 54-59.

APPENDIX 1

EFFUSION FORMULA

The following derivation of the effusion formula is similar to that presented by St. Clair and Spendlove.[6][7] Their derivation is supplemented by information from Loeb.[8]

Probability theory indicates that the chance P_s of a particular molecule striking the walls of the container in a time interval of one second when the area of the walls is S square centimeter is

$$P_s = SC/4V \qquad (A)$$

where

C is the average velocity in cm/sec, and

V is the volume of container in cm^3.

If there are N_t molecules in the container with volume V cm^3, the number, N_s, striking the walls per second is given by $N_s = P_s N_t$. Thus, $N_s = N_t SC/4V$, and calling $N_t/V = N$, the number of molecules per cubic centimeter, $N_s = SNC/4$. If $N_s/S = n$, the number striking a square centimeter per second, then

$$n = NC/4 \qquad (B)$$

The kinetic theory of gases may be used to derive a relationship between the rate of evaporation and the vapor pressure. For a gas composed of molecules with mass m and an average velocity C, the number of molecules passing through a cross section of one square centimeter per second is given by equation (B). The weight w of a substance striking

a square centimeter per second is given by

$$w = mn = NmC/4 \qquad (C)$$

where N is the number of molecules per cubic centimeter of gas. Since Nm is the weight of the molecules per cubic centimeter it is equal to the density, ρ , of the gas. Using the ideal gas law gives

$$\rho = Nm = M/V = pM/RT \qquad (D)$$

where

p is the pressure of the gas in dynes/cm^2,

V is the volume in cm^3,

M is the molecular weight in gms,

R is the gas constant in ergs per mole per degree, and

T is the absolute Kelvin temperature.

The root-mean-square velocity, designated by u, is

$$u = (3p/\rho)^{1/2} \qquad (E)$$

The average velocity, according to the Maxwell distribution law, is equal to

$$C = u(8/3\pi)^{1/2} \qquad (F)$$

Using (D) and (E) in (F) gives

$$C = (8RT/\pi M)^{1/2} \qquad (G)$$

Substituting equations (D) and (G) into equation (C) gives the following expression, known as the effusion formula,

$$w = p(M/2\pi RT)^{1/2} \qquad (H)$$

w is the weight of gas striking one square centimeter of surface per second when the gas is at pressure p and temperature T.

If the vapor pressure, p, at any given temperature is known, it may be used in equation (H) to calculate the rate of evaporation of a substance into a vacuum. Under these conditions, molecules evaporating from the surface do not collide with other molecules and return to the liquid phase. This rate of evaporation will be the theoretical maximum rate.

The expression for the maximum rate of evaporation can be simplified by inserting the values of the constants in equation (H) to obtain

$$w = p(M/2\pi RT)^{1/2} = p\left[M/(2)(3.14)(8.314)(10^7)T\right]^{1/2}$$
$$= (43.74)(10^{-6})(p_o)(M/T)^{1/2}$$

where

w is the maximum rate of evaporation in gms/cm^2-sec, the rate of evaporation into a perfect vacuum,

T is the temperature in degrees °K,

p is the vapor pressure of evaporating liquid at temperature T in dynes/cm^2, and

M is the molecular weight of the liquid in grams.

Using the molecular weight of zinc and converting units gives

$$w_o = (43.74)(10^{-6})(13.59)(980)(60)(p_o)(65.38/T)^{1/2}$$
$$= 28.30p_o/T^{1/2}$$

where

w_o is the rate of evaporation of zinc in gms/cm^2-min, and

p_o is the vapor pressure of zinc at temperature T in mm Hg.

APPENDIX 2

CALCULATION OF THE RATE OF EVAPORATION

The rate of evaporation of zinc into an atmosphere containing argon as the residual gas with the total pressure equal to one atmosphere and the liquid zinc at 650°C is calculated below.

Epstein equation:

The Epstein equation is given as

$$w_1 = \frac{2.736\ w_o T\ (1/b)^{2/3}}{\lambda\ P} \qquad \frac{(1 + M_{Zn}/M_{Ar})^{1/2}}{\left[1 + (\rho Zn/\rho Ar)^{1/3}\right]^2} \qquad (6)$$

w_o is obtained from equation (2) on page :

$$w_o = 28.30\ p_o/T^{1/2} \qquad (2)$$

The vapor pressure of zinc at 650°C is calculated from equation (3).

$$\log p_o = -6754.5/T - 1.318 \log T - 0.0601 \times 10^{-3} T + 12.723 \qquad (3)$$

and $p_o = 27.70$ mm Hg.

Then $w_o = (28.30)(27.70)/(923)^{1/2} = 25.80$ gms/cm^2-min.

In equation (6)

$w_o = 25.80$ gms/cm^2-min

$T = 923°K$

$\lambda = 7.5$ cms, the distance from the end of the condenser to the middle of the bath

$P = 1$ atm $= (76)(13.60)(980)$ dynes/cm^2

$b = 32.19$ cm^3/mole [16]

$M_{Zn} = 65.38$ gms

M_{Ar} = 39.94 gms

$\rho Z_n = p_o M_{Zn}/RT = (27.70)(65.38)/(R)(923)$
$\rho Ar = (760 - p_o)\ M_{Ar}/RT = (732.30)(39.94)/(R)(923)$

Inserting these values into equation (6) gives

$$w_1 = 0.000114 \text{ gm/cm}^2\text{-min.}$$

Luchak-Langstroth equation:

The Luchak-Langstroth equation was:

$$w_2 = (9.60)(10)^{-4}(p_o)(M_{Zn}D/T\lambda) \qquad (7)$$

Maxwell's equation was used to calculate the diffusivity. This was given as:

$$D = \frac{kT^{3/2}}{P(V_{Zn}^{1/3} + V_{Ar}^{1/3})^2}\ (1/M_{Zn} + 1/M_{Ar})^{1/2} \qquad (8)$$

The following values were used in equation (8) to obtain the diffusivity:

k = 0.0047. This is the largest possible value of k[13] and was was selected to obtain the best agreement with the experimental results,

T = 923°K,

P = 1 atm,

V_{Zn} = 65.38/6.7 = 9.75 cm^3/mole, [17]

V_{Ar} = 39.94/1.4 = 28.44 cm^3/mole, [17]

M_{Zn} = 65.38,

M_{Ar} = 39.94.

Equation (8) then gives

$$D = 0.974 \text{ cm}^2/\text{sec.}$$

The values of the other variables in equation (7) have been give above and were used with this value of D to give

$$w_2 = 0.000244 \text{ gm/cm}^2\text{-min}$$

Maxwell-Stefan equation:

The Maxwell-Stefan equation was given as:

$$w_3 = \frac{(60)(P)(M_{Zn})(D)(p_{Zn650^\circ} - p_{Zn20^\circ})}{(\lambda)(R)(T)(p_{Ar20^\circ} - p_{Ar650^\circ})} \ln \frac{p_{Ar20^\circ}}{p_{Ar650^\circ}}$$

The appropriate values of the variables in this equation are

$P = 1$ atm,

$M_{Zn} = 65.38$,

$D = 0.974$ cm^2/sec from above calculation,

$p_{An650^\circ} = 27.70/760 = 0.0364$ atm,

$p_{Zn20^\circ} = 0$ atm,

$p_{Ar20^\circ} = 1$ atm,

$p_{Ar650^\circ} = 1 - p_{Zn650} = 1 - 0.0364 = 0.964$ atm,

$\lambda = 7.5$ cms,

$R = 82.0$ cm^3-atm/degree-gm mole,

$T = 923^\circ$K.

These values give

$w_3 = 0.000252$ gm/cm^2-min.

APPENDIX 3

CALCULATION OF RELATIVE FORCES EXERTED BY RESIDUAL GASES

The root-mean-square velocity of a gas is a function of its temperature and atomic or molecular weight only because the kinetic energy of every gas is the same at a given temperature.

Equation (10) was used to calculate the root-mean-square velocity

$$u = \sqrt{3RT/M} \qquad (10)$$

The proper value of the gas constant to use in this equation is 8.3×10^7 ergs/g.mole-degree. The temperatures and molecular weights used and the resulting root-mean-square velocities were

Gas	Temperature, °C	Mole Weight grams	u, cms/sec
Zn	850	65.38	6.54×10^4
Zn	750	65.38	6.20×10^4
Ar	850	39.94	8.37×10^4
Ar	750	39.94	8.00×10^4
CO	850	28.00	10.0×10^4
H_2	750	2.00	35.8×10^4

These molecular weights and root-mean-square velocities were used in equations (11) and (12) to obtain the final velocity of the zinc atoms after head-on collisions with the residual gas. In this calculation the initial velocity of the zinc atom was always taken to be positive and that of the residual gas to be negative. Equation (13) was used to calculate the change of momentum for the zinc atoms. The results of these calculations were

Residual Gas	Temperature °C	u'_{Zn} cms/sec	Change in Momentum, g-cm/sec
Ar	850	-4.75×10^{4}	7.38×10^{6}
CO	850	-3.36×10^{4}	6.47×10^{6}
Ar	750	-4.70×10^{4}	7.16×10^{6}
H_2	750	$+3.79\times10^{4}$	1.62×10^{6}

Equation (14) was used to calculate the number of collisions per unit volume per second. In this equation the number of atoms or molecules per cubin centimeter was determined from

$$n_i = \frac{6.023\times10^{23}}{22,400}\left(\frac{p_i}{760}\right)\left(\frac{273}{T}\right)$$

where

n_i is the number of atoms per cm^3,

6.023×10^{23} is Avogadros number,

22,400 is the volume of one mole at standard conditions,

p_i is the partial pressure of gas i. p_i was obtained from equation (3) when i was Zn and $p_i = 760 - p_{Zn}$ when i was the residual gas.

The atomic diameters were taken from Loeb[8], and the other variables have been given above. The atoms or molecules per unit volume, the atomic or molecular diameters and the number of collisions obtained from these calculations were:

Residual Gas	Temp., °C	p_{Zn}, mm Hg	n_{Zn}, cm^{-3}	n_G, cm^{-3}	σ_{Zn}, cm	σ_G, cm	Z_{Zn-G}, cm^{-3}-sec^{-1}
Ar	850	418.43	3.59×10^{18}	2.53×10^{18}	2.9×10^{-8}	3.36×10^{-8}	3.19×10^{27}
CO	850	418.43	3.59×10^{18}	2.53×10^{18}	2.9×10^{-8}	3.50×10^{-8}	3.72×10^{27}
Ar	750	123.87	1.16×10^{18}	6.00×10^{18}	2.9×10^{-8}	3.36×10^{-8}	2.00×10^{27}
H_2	750	123.87	1.16×10^{18}	6.00×10^{18}	2.9×10^{-8}	2.32×10^{-8}	5.26×10^{27}

The product of the number of collisions per unit volume per second and the change in momentum of a zinc atom in a head-on collision with the residual gas atom or molecule, $F_{Zn,G}$, was calculated according to equation (15).

Residual Gas	Temperature °C	$F_{Zn,G}$ dynes/cm^3
Ar	850	2.35×10^{34}
CO	850	2.12×10^{34}
Ar	750	1.43×10^{34}
H_2	750	0.84×10^{34}

APPENDIX 4

LIST OF SYMBOLS

English Letter Symbols

C	average velocity
D	diffusivity
$F_{Zn,G}$	factor proportional to force exerted by residual gas G on zinc atoms escaping from the liquid phase
M	molecular weight
M_A	molecular weight of metal A
M_B	molecular weight of residual gas B
M_{Ar}	molecular weight of argon
M_{Zn}	molecular weight of zinc
N	number of molecules per cubic centimeter
N_s	number of molecules striking the walls per second
N_t	total number of molecules in the container
P	total pressure
P_s	chance of a particular molecule striking the walls if the container in a time interval of one second
R	gas constant
S	area of the walls
T	absolute temperature
T_{A1}	the absolute temperature of the metal A at the evaporating surface
T_{A2}	the absolute temperature of the metal A at the condensing surface
V	total volume
V_A	molal volume of metal A in liquid state at its normal boiling point

V_B	molal volume of the residual gas B in liquid state at normal boiling point
V_{Zn}	molal volume of zinc in liquid state at its normal boiling point
Z_{Zn-G}	number of collisions per unit volume per second between zinc vapor atoms and residual gas atoms or molecules
b	van der Waal's constant
k	constant for diffusivity equation
m	mass of molecule
n	number of molecules striking a square centimeter of surface per second
n_G	number of residual gas atoms or molecules per cubic centimeter
n_i	number of atoms or molecules per cubic centimeter
n_{Zn}	number of zinc vapor atoms per cubic centimeter
p	pressure of gas or vapor
p_{A1}	partial pressure of the metal A at the evaporating surface
p_{A2}	partial pressure of the metal A at the condensing surface
p_{B1}	partial pressure of the residual gas B at the evaporating surface
p_{B2}	partial pressure of the residual gas B at the condensing surface
p_{BM}	log mean partial pressure of the residual gas B
p_i	partial pressure of residual gas i
$p_{Pb(g)}$	partial pressure of lead in the vapor phase
p_r	partial pressure of zinc vapor contact with the liquid surface during evaporation
p_{Zn}	partial pressure of zinc vapor
$p_{Zn(g)}$	partial pressure of zinc in the vapor phase
p_o	vapor pressure of zinc

p	partial pressure of zinc in the vapor phase
p	vapor pressure of zinc
	root mean square velocity
u_{Zn}	root means square velocity of zinc atom before head-on collision
u'_{Zn}	root mean square velocity of zinc atom after one head-on collision
w	rate of evaporation
w'	rate of zinc vapor moving back onto liquid surface
w_A	maximum rate of evaporation of metal A
w_n	net rate of evaporation of zinc
w_o	maximum rate of evaporation of zinc
w_1	Epstein rate of evaporation
w_2	Luchak rate of evaporation
w_3	Maxwell rate of evaporation
$x_{Pb(g)}$	Mole fraction of lead in the vapor phase
$x_{Pb(1)}$	Mole fraction of lead in the liquid phase
$x_{Zn(g)}$	Mole fraction of zinc in the vapor phase
$x_{Zn(1)}$	Mole fraction of zinc in the liquid phase

Greek Letters Symbols

λ	distance between evaporating and condesning surfaces
π	3.14
ρ	density
ρ_A	density of metal vapor A
ρ_{Ar}	density of argon
ρ_B	density of residual gas B
ρ_{Zn}	density of zinc vapor
σ_G	diameter of residual gas atom as molecule
σ_{Zn}	diameter of zinc vapor atom

VITA

The author was born in Taiwan, Republic of China, on August 25, 1936. His high school education was completed in 1955 at Provincial Kaohsiung High School. In September 1955, he entered Cheng Kung University, located in Tainan. After graduation with a B. S. degree in Metallurgical Engineering in June, 1959, he worked for the Taiwan Metal Mining Corporation for two and one half years.

He has been enrolled in the Graduate School of the University of Missouri at Rolla since September, 1964.